9th International Interdisciplinary Congress on Renewable Energies, Industrial Maintenance, Mechatronics and Informatics

Booklets

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Title: Determination of the risk level from btex inhalation at a gas station in Ciudad del Carmen, Campeche

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Editorial label ECORFAN: 607-8695
BCIERMMI Control Number: 2024-01
BCIERMMI Classification (2024): 241024-0001
RNA: 03-2010-032610115700-14
Pages: 15

CONAHCYT classification:
Area: Physics-Mathematics and Earth Sciences
Field: Earth and space sciences
Discipline: Climatology
Subdiscipline: Atmospheric pollution

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PRESENTATION CONTENT

Introduction

Methodology

Results

Conclusions

References

INTRODUCTION

Volatile organic compounds (VOCs) are a group of chemical compounds emitted from highly volatile liquids at room temperature and from industrial processes (FAO & UNEP, 2022). These compounds and their reaction products pose an unacceptable risk to public and occupational health and biological and physical environments (Bloemen & Burn, 1993). Studies worldwide have reported that BTEX (benzene, toluene, ethylbenzene, and the three isomers of xylene) are potentially dangerous for the environment and human health (Campos-Candel, Llobat-Estelles & Mauri-Aucejo, 2007).

While these compounds can be released from natural sources like forest fires, the majority are emitted by human-related activities such as oil and natural gas extraction and combustion, petrochemical activities, and various industrial processes. Due to their volatile nature, humans are primarily exposed to VOCs through inhalation. Both chronic and acute exposure can have serious health consequences, including neurological diseases, cancer, and teratogenic effects (ATSDR, 2004; Baghani et al, 2024; Chaiklieng et al, 2024; Hosseinpour et al, 2024; Ma et al, 2024; Sadeghi Amin, S. & Nasrabadi, T. (2024).

The presence of BTEX compounds in the atmosphere is concerning because there are no established maximum limits for these pollutants. As a result, there is a lack of continuous or systematic measurements of these contaminants in Mexico. To address this, we need to establish a theoretical framework by reviewing the available regulatory standards and examining results from other national and international studies. Criterion pollutants have well-established limits and extensive information on their sources and health impacts.

METHODOLOGY
STUDY AREA

The study site is located in the State of Campeche, in the southeastern region of Mexico. It shares borders with the State of Yucatan to the North, the state of Quintana Roo and Belize to the East, the Republic of Guatemala to the South, and the state of Tabasco and the Gulf of Mexico to the West. The state covers an area of 57,507 km2 and has a total population of 928,363 inhabitants, which represents 0.7% of the country's total population (INEGI, 2020). Ciudad del Carmen is the main city in the municipality of Carmen, in the state of Campeche. It is situated in the Southwestern part of the Yucatan peninsula, on the Western side of the Island of Carmen, between the Gulf of Mexico and the Terminos Lagoon. In this study, we will assess the levels of BTEX in the ambient air of an area affected by urban and oil activities in the municipality of Carmen, Campeche. The sampling site was chosen at a service station (gas station) that is frequently visited by motorists and other means of transportation. The sampling site's location is presented in Figure 1.

Figure 1
Location of the sampling site

METHODOLOGY
SAMPLING

Active sampling of ambient air was conducted using the "Determination of aromatic hydrocarbons (benzene, toluene, ethylbenzene, p-xylene, 1, 2, 4-trimethylbenzene) in air - Activated carbon adsorption method/Gas chromatography" method, which is approved by the National Institute of Safety and Hygiene at Work (INSHT) (MTA/MA-030/A92) (INSHT, 1995). A total of 30 samples of ambient air were gathered in glass tubes containing activated carbon brand 226-01 Anasorb CSC from SKC. These tubes are 7 cm in length, with an external diameter of 6 mm and an internal diameter of 4 mm. Each tube contains two sections of activated carbon separated by a 2 mm portion of polyurethane foam (see Figure 2). Ambient air was drawn through a GAST-type vacuum pump at a controlled flow rate of 200 ml/min through horizontally placed tubes. The ends of both sections were broken, and section 2 (containing 50 mg of activated carbon) was securely positioned on a rubber or plastic tube holder of suitable length and diameter. The tube was covered with aluminum foil to prevent photochemical reactions and interference when reading the samples.

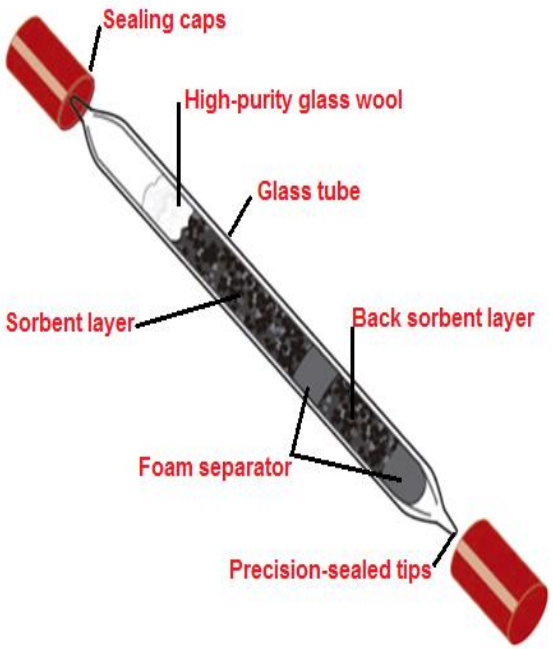


Figure 2
Characteristics of the active sampling tubes

METHODOLOGY
SAMPLING

The process of obtaining ambient air samples was conducted during three time periods based on diurnal variation: morning B1 (7:00 a.m. to 8:00 a.m.), midday B2 (12:00 p.m. to 1:00 p.m.), and afternoon B3 (5:00 p.m. to 6:00 p.m.), each lasting 1 hour. A total of 30 samples were collected over 10 sampling days in the 2024 dry season. After each sampling, the tubes were covered, labeled, and stored in special bags to prevent direct sunlight exposure and potential photochemical reactions. Subsequently, they were refrigerated to preserve them for no more than 20 days until analysis at the Environmental Protection laboratory of the Autonomous University of Carmen (UNACAR).

CHEMICAL ANALYSIS

The chemical analysis was conducted at the Environmental Protection Laboratory of the Autonomous University of Carmen following the method established by the National Institute of Safety and Hygiene of Spain MTA/MA-030/A92 (INSHT, 1995). Calibration curves were prepared using reagent-grade solutions of 99.98% purity from the Sigma-Aldrich brand. After this, chemical desorption was carried out, by using 2 ml amber vials with lids and septa. These vials were labeled and subjected to pre-treatment by rinsing with distilled water and then dried. A small amount of HPLC-grade carbon disulfide was added as an adsorbent reagent, allowing it to dry to avoid contamination of the samples with impurities. After pre-treatment, desorption was carried out by carefully breaking the end of section 1 of the tube to remove the glass wool using a metal clamp. The material was then emptied into the vial, and 2 ml of CS_2 was added. The vial was closed, and the steps were repeated for section 2 and for each sample. After closing the vials, they were shaken vigorously for 5 minutes and refrigerated for a maximum of 24 hours before analysis by gas chromatography.

METHODOLOGY
STATISTICAL ANALYSIS

Statistical analysis on the BTEX concentration data and meteorological data was conducted by using the Excel statistical package XLSTAT version 2019. Several statistical tools were using, including: 1. Pearson correlation to identify relationships between BTEX, criterion pollutants, and meteorological variables; 2. Principal component analysis (PCA) to explain the variance and discover the structure of the data set. PCA results help identify whether a contaminant is secondary or primary, or to identify the specific source of the contaminants; 3. Friedman non-parametric tests ($\alpha = 0.05$) to evaluate the differences between the sampling periods of the concentrations of atmospheric pollutants measured. This helps determine whether the data studied come from the same population and if there is significant diurnal variation;
4. Box plot to display the descriptive statistics of the results obtained, including the concentrations, means, maximum, and average of each of the aromatic hydrocarbons. This allows for easy identification of the contaminant with the highest average concentrations and any diurnal pattern or trend during sampling.

METEOROLOGICAL ANALYSIS

Wind analysis was performed to determine the places where the BTEX emissions probably came from. Windrose program and Google Earth were used to create wind roses and to identify potential emission sources based on wind direction over ten sampling days. Then, Excel was used to estimate the average wind direction during morning, afternoon, and night for the sampling period. Additionally, the HYSPLIT trajectory model from the National Oceanic and Atmospheric Administration (NOAA) was applied to estimate air mass trajectories and to identify regional influences. Finally, spider web plots were obtained to visually represent the possible origin of BTEX concentrations (NOAA, 2024).

METHODOLOGY
HEALTH RISK ANALYSIS

The carcinogenic potential of benzene is well known (Moolla et al., 2015). The European Union recommends an annual limit of 5 µg m^{-3} for benzene in ambient air, while the USEPA establishes a value of 4.0 ppbV for this contaminant (US EPA, 2012). To determine the daily exposure (E), the cancer risk potential (LTCR), and the non-cancer risk potential (HQ), we used the methodology proposed by Zhang et al. (2012). The daily exposure (mg/kg per day) of an individual by inhalation can be calculated as follows:

$$E = \frac{C * Ira * Da}{Bwa} \qquad [1]$$

Where:
C (mg/m^3), is the mean concentration of benzene
Ira, is the inhalation rate for an adult person (0.83 m^3/hr) (US EPA, 1998)
Da, is the exposure duration for an adult (24 hr/día)
Bwa, is the mean weight for an adult -- 65 kg -- (US EPA, 1998)

In addition, the lifetime cáncer risk (LTCR) is calculated as follows:

$$LTCR = E * SF \qquad [2]$$

Where:
E, is the daily exposure for a person by inhalation
SF, is the slope factor for benzene toxic inhalation risk when considering the linear carcinogenic effect due to exposure. The proposed SF value for benzene (0.029 kg/mg per day) was based on US EPA 2012.

METHODOLOGY
HEALTH RISK ANALYSIS

Finally, the non carcinogenic risk of BTEX was estimated as a risk quotient (HQ):

$$HQ = \frac{C}{Rfc} \qquad [3]$$

Where:
C, is the daily mean concentration (µg/m^3)
Rfc, is the reference concentration of inhalation, proposed by U.S. EPA for benzene (0.03 µg/m^3), toluene (5 µg/ m^3), ethylbenzene (1 µg/m^3) and xylene (0.1 µg/m^3) (USEPA, 2012).

RESULTS

For al BTEX concentrations, it was evident that were significantly higher during sampling period B1, which corresponds to the time from 07:00 to 08:00 hrs.

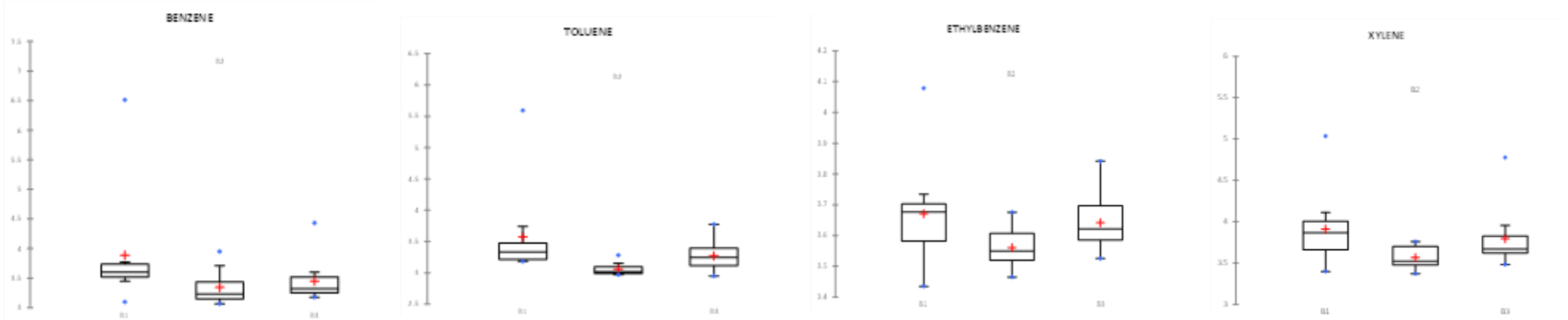


Figure 3
Diurnal variability of BTEX

RESULTS

It was found that the prevailing wind direction was from SE

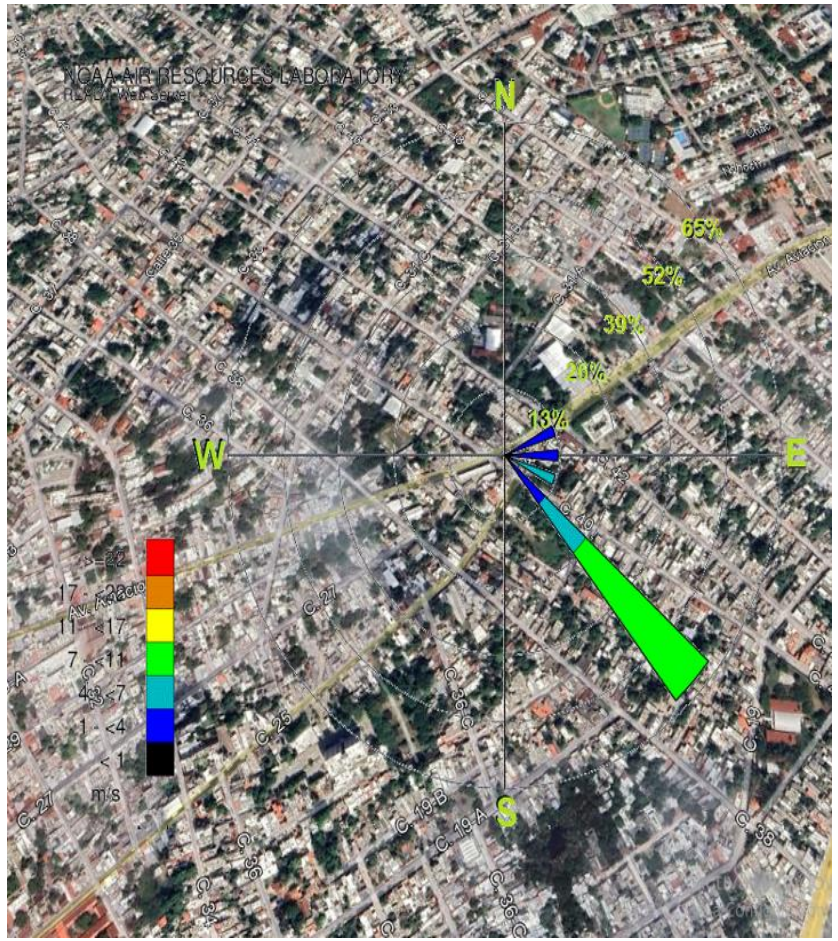


Figure 4
Wind rose for the study period in the sampling site

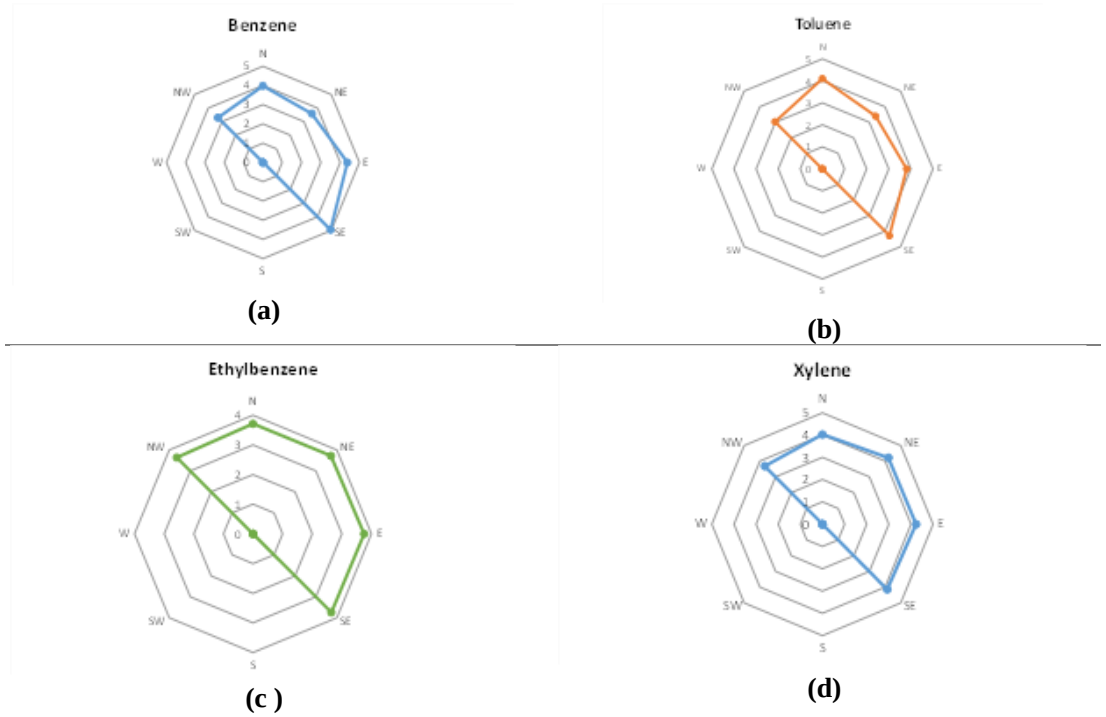


Figure 5
Concentration rose in the study area for each BTEX compound

RESULTS

To identify significant correlations between the BTEX compounds and the meteorological variables, we conducted a bivariate analysis using Pearson correlation.

Variables	Benzene	Toluene	Ethylbenzene	Xylene	Temperature	Pressure (Hpa)	Humidity
Benzene	1	0.972	0.825	0.868	-0.982	-0.277	0.789
Toluene	0.972	1	0.934	0.960	-0.999	-0.493	0.910
Ethylbenzene	0.825	0.934	1	0.997	-0.917	-0.772	0.998
Xylene	0.868	0.960	0.997	1	-0.946	-0.717	0.990
Temperature	-0.982	-0.999	-0.917	-0.946	1	0.454	-0.891
Pressure (Hpa)	-0.277	-0.493	-0.772	-0.717	0.454	1	-0.809
Humidity	0.789	0.910	0.998	0.990	-0.891	-0.809	1

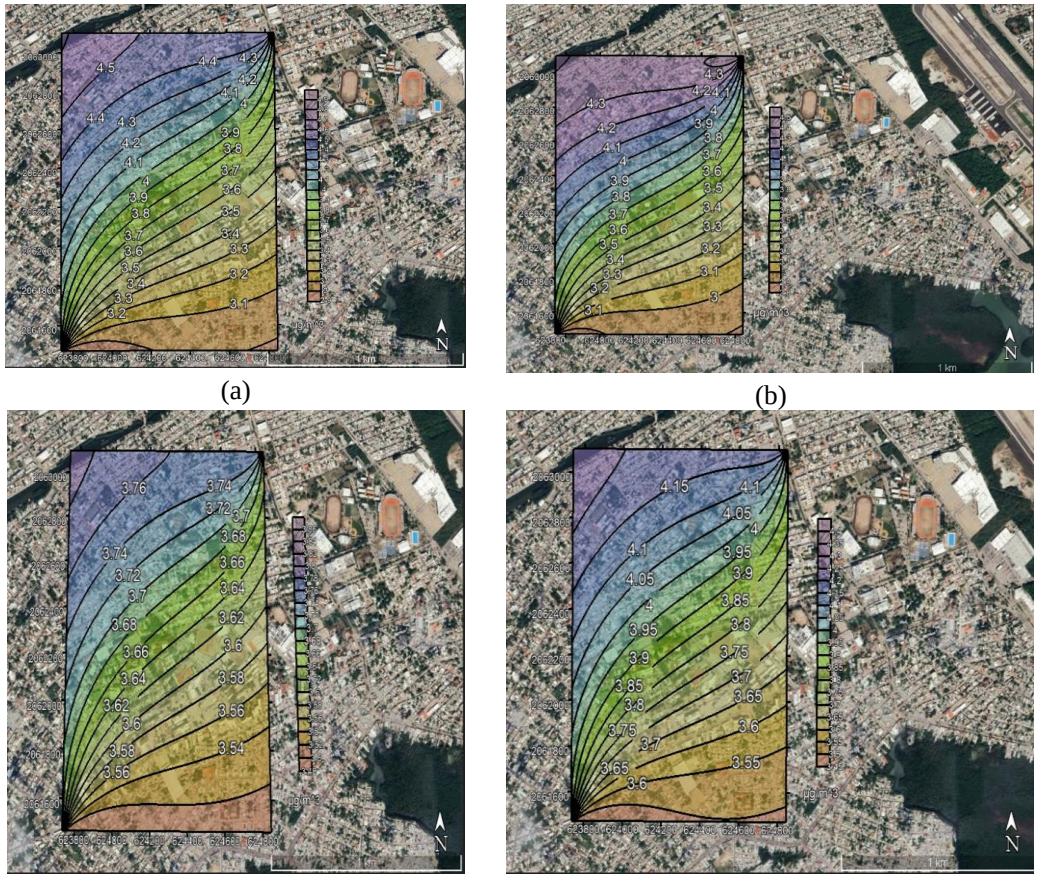
Table 1
Bivariate analysis

we observed the following significant correlations: toluene-benzene (0.972), benzene-ethylbenzene (0.825), toluene-ethylbenzene (0.934), benzene-xylene (0.868), toluene-xylene (0.960), and xylene-ethylbenzene (0.997). It's important to note that the correlation between BTEX compounds in ambient air can vary based on factors such as emission sources, atmospheric conditions, and geographic location. These volatile organic compounds (VOCs) are commonly found in the air due to industrial, automotive, and other human-made sources.

BTEX compounds can be released into the air during processes such as incomplete combustion of fossil fuels, vehicle emissions, and various industrial activities. The correlation between these compounds may differ depending on the emission source. For instance, in urban areas with heavy traffic, the correlation is likely to be higher due to vehicle emissions. However, in industrial areas where toluene-containing solvents are used, the correlation may be different. It's crucial to note that although BTEX compounds may be correlated in certain situations, they may also have independent emission sources and different atmospheric behaviors. Additionally, each compound has different effects on human health.

RESULTS

From biplot of the PCA analysis, there was noticeable clustering between BTEX compounds and humidity, as well as a significant inverse correlation between BTEX compounds and temperature. Additionally, there is a significant inverse correlation between atmospheric pressure and xylene, ethylbenzene, and humidity.



(a) (b) (c) (d)

Figure 6
BTEX maps for the study area

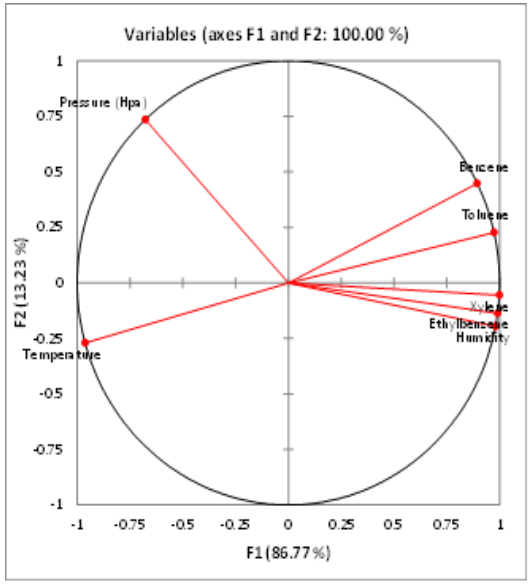


Figure 7
PCA biplot

The BTEX concentrations were determined using the Kriging method to create a new set of estimated data. These estimates were then used to create concentration isolines in Surfer. The isolines were georeferenced to produce maps showing the spatial distribution of each BTEX compound.

RESULTS

The spatial distribution of benzene is depicted in Figure (a), indicating higher concentrations towards the northwest of the sampling area, specifically near the fishing port, North Beach, and a section of the city center. This area also encompasses the Atasta sour gas recompression station and the offshore platform region. Similarly, Figure (b) displays the spatial distribution of Toluene, revealing a similar pattern. Figure (c) illustrates the spatial distribution of ethylbenzene, indicating that ethylbenzene concentrations were higher toward the northwest of the sampling area, specifically near the North Beach, Fishing Port, and City Center area. Conversely, Figure (d) demonstrates the spatial distribution of xylene, displaying a similar spatial pattern to the other BTEX compounds.

The B/T and X/E ratios can help determine the likely origin of BTEX at a specific site. A toluene/benzene ratio (B/T) of less than 2-3 indicates a high influence of vehicular emissions, suggesting that BTEX comes from motor vehicle emissions, as both toluene and benzene are present in gasoline. On the other hand, in the case of the xylene/ethylbenzene (X/E) ratio, this ratio is used to estimate the age of air masses and to infer whether the emissions are local and come from fresh emissions, or if they come from aged air masses, that is, of regional nature and with a certain history of photochemical processing. This way, values below 4.4 in this ratio indicate that the air masses are recent and carry fresh emissions, so their origin can be considered local. The B/T ratios for the 3 sampling times (B1, B2, and B3) from Table 8 were equal to or greater than 1, indicating a high influence of vehicular emissions at the sampling sites. This suggests that BTEX emissions likely originated from vehicular sources, possibly even from the same service station where the sampling was conducted.

Table 2
B/T ratios

B/T		
B1	**B2**	**B3**
1.0162	1.0417	1.0209
0.9499	1.0250	1.0218
1.0765	1.0576	1.0383
1.0895	1.0510	1.0230
1.1019	1.0677	0.9286
1.1065	1.1298	1.0239
1.0953	1.0758	1.1047
1.1298	1.0669	1.0639
1.0823	1.2516	1.1733
1.1644	1.1543	1.1448
1.0812	**1.0921**	**1.0543**

RESULTS

It was evident that the X/E ratios for the 3 sampling times (B1, B2, and B3) were close to 1. This suggests that these are recent air masses carrying fresh emissions, indicating that the BTEX compounds measured can be considered to have a local origin.

The B/T ratios are used to determine the relative abundance between vehicular and non-vehicular sources. In this case, the B/T ratios for the sampling site were less than 3, ranging from 0.998 to 1.168 with an average value of 1.076. This indicates that BTEX emissions come from vehicular sources, as this range has been reported in various urban areas worldwide

Table 3
X/E ratios

X/E		
B1	**B2**	**B3**
0.9894	0.9732	0.9934
0.9869	0.9827	1.0101
1.0152	1.0142	1.0340
1.0762	0.9863	0.9882
1.1099	0.9887	1.0462
1.0736	1.0395	1.0050
1.0595	1.0132	1.2433
1.0401	0.9864	1.0041
1.0411	1.0289	1.0662
1.2343	0.9988	1.0114
1.0626	**1.0012**	**1.0402**

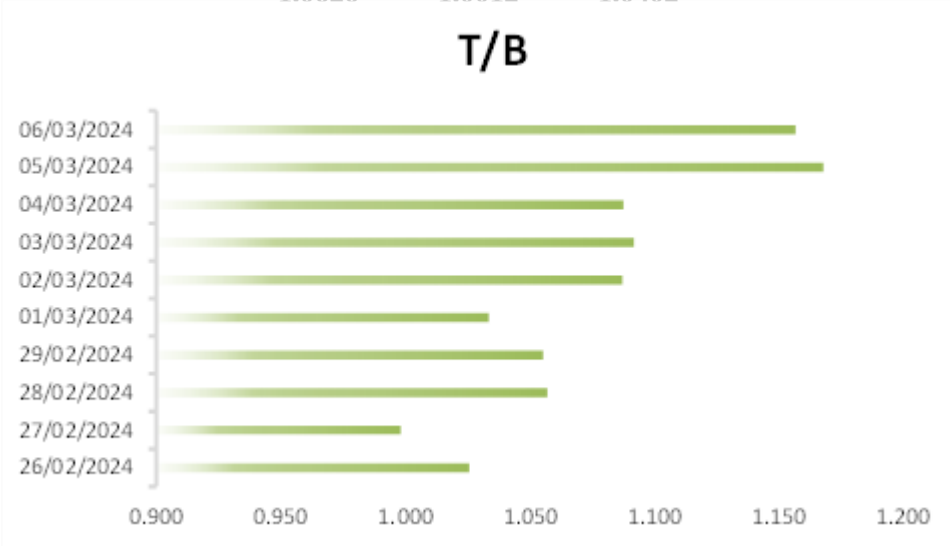


Figure 8
T/B ratios

RESULTS

The X/E ratios are used as an indicator of the photochemical age of the air masses at the sampling site. This is because xylene is more reactive compared to ethylbenzene, leading to photochemical reactions. In this study, the X/E ratios indicate that the air masses are fresh

The cancer risk index due to exposure to benzene at the sampling site was calculated for both, adult and child populations. Lifetime cancer risk (LTCR) values for the sampling site were from $2.88x10^{-5}$ to $4.12x10^{-5}$, with a mean value of $3.25x10^{-5}$ for adults; and $5.45x10^{-5}$ to $7.8x10^{-5}$ with a mean value of $6.15x10^{-5}$ for children. The averages in both cases can be seen to exceed the reference value proposed by the US EPA (LTCR $1x10^{-6}$); being the risk significantly higher for the child population.

Non-carcinogenic risk quotients were estimated for the BTEX compounds. The overall potential for non-carcinogenic effects due to exposure to more than one chemical was determined as an HQ risk quotient, where a value of HQ <1 indicates that the population is not exposed to a significant risk of contracting diseases other than cancer (respiratory and cardiovascular diseases) as a consequence of daily exposure to this type of compounds. The HQ values were in all cases less than unity, which suggests that the population near the study area does not present a risk of suffering respiratory and cardiovascular diseases.

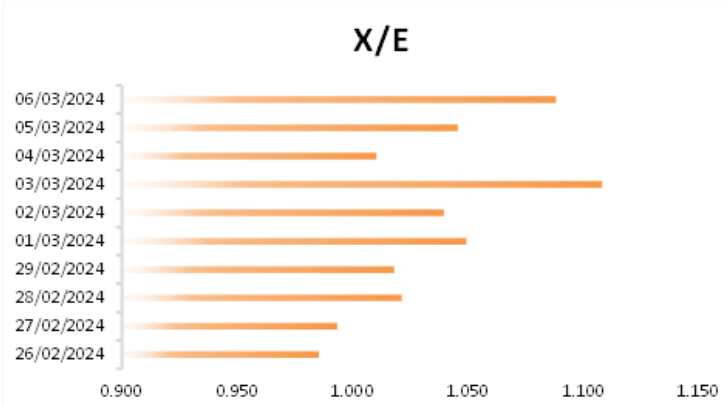
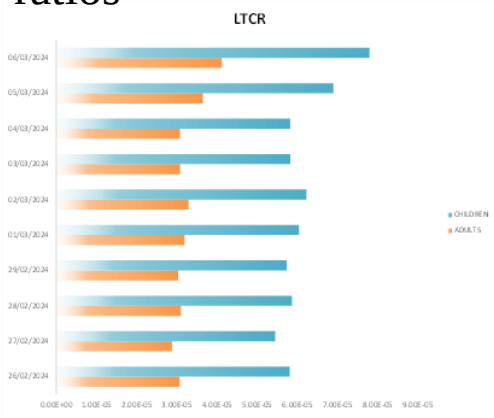
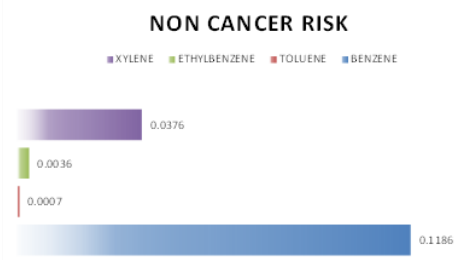


Figure 9
X/E ratios



(a)



(b)

Figure 10
Cancer Risk

Figure 11
Non Cancer Risk

CONCLUSIONS

Temporal variability in BTEX levels was evaluated at a site adjacent to a gas station in Ciudad del Carmen, Campeche, during the dry season of 2024. The concentrations of all BTEX were highest during the B1 sampling period, which corresponds to the time from 07:00 to 08:00 hrs; However, when applying hypothesis tests, it was found that these differences were only significant for toluene. From plots of wind vs concentration, it was assessed the influence of surface meteorology on the measured BTEX levels, regarding this, it was found that the trend was the same for all BTEX compounds, with the highest concentrations when the wind had a SE component, that is, when the wind blew from the SE to the NW.

To determine whether vehicular sources had a significant impact on the emission of BTEX compounds, the B/T and X/E ratios were estimated. The B/T ratios for the 3 sampling times (B1, B2, and B3) were close to 1, which can be considered characteristic of sites with a high influence of vehicle emissions. Therefore, we conclude that BTEX emissions had their origin in vehicular emissions and, also from the service station where the sampling was done. On the other hand, since the X/E ratios are used as an indicator of the photochemical age of the air masses at the sampling site, in this study, all cases, in a range of 0.998 to 1.168 with an average value of 1.076, which indicates that the emissions were recent and of local origin, indicating that they are fresh air masses.

Finally, the cancer risk index for benzene exposure exceeded the reference value proposed by the US EPA (LTCR $1x10^{-6}$), suggesting a significant risk, and being even higher for the child population. The overall potential for no carcinogenic effects due to BTEX exposure was determined as an HQ risk quotient. In all cases, a value of HQ<1 was obtained, indicating that the population is not exposed to a significant risk of contracting diseases other than cancer (respiratory and cardiovascular diseases) due to the daily exposure to the BTEX levels found in the study area. However, it is necessary to carry out more studies around the city including other climatic seasons and a greater number of sampling sites (service stations) to obtain more precise conclusions regarding the risk associated to this type of emissions.

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